A Combined Density Functional Theory and Monte Carlo Approach for Quantifying Catalytic Energies in a Liquid Environment

Completed Technology Project (2014 - 2018)

Project Introduction

The primary goals of this project are to develop a method for determining the equilibrium concentration of metal catalysts under actual conditions of liquid phase reactions and to use this method to determine the optimal catalyst alloy for a given system based on chemical reaction kinetics using computational simulations. While most previous computational research on heterogeneous catalysis has focused on gas phase reactions on pure metal catalysts, several groups have begun looking at effects of the reaction environment including solvation effects and adsorbate coverage effects. Studies have been conducted analyzing solvation effects for single adsorbate cases while other studies have analyzed the effects of adsorbate coverage for heterogeneously catalyzed gas phase reactions, and both effects have been shown to be significant independently. However, to date, no group has included both of these effects concurrently. The proposed project aims to develop a method to efficiently analyze the simultaneous effects of solvation and adsorbate coverage on each other as well as the reaction energy. This study will be accomplished by using the Vienna Ab initio Simulation Package (VASP) implementation of Density Functional Theory (DFT) to calculate the interaction energies between solvent molecules, coadsorbed molecules, and adsorbed reactants. These interaction energies will then be used to determine the equilibrium concentrations of the adsorbed reactants. The absorption of these adsorbates into the metal lattice and their subsequent interactions with metal atoms to form metal complexes, which may be more or less catalytically active than the pure metal, will then be studied. Grand canonical Monte Carlo codes will be written to ensure sufficient ensembles are sampled for all phase equilibria calculations, including absorption and the subsequent absorption of the adsorbate molecules. Finally the equilibrium metal/metal complex composition will be used to determine reaction kinetics parameters for the rate-limiting anode reaction. This will allow for a comparison based on the starting catalyst alloy and enable us to suggest more cost-effective catalyst candidates. The specific system of interest will be the rate-limiting anode reaction of direct methanol fuel cells (DMFCs), the oxidation of carbon monoxide by hydroxide to form carboxylic acid, due to the aqueous reaction environment and wealth of previous literature data to compare to simulation results. This work will prove significant because it will yield a method that will be able to yield simulation results that provide a more accurate picture of molecular scale phenomena affecting heterogeneous catalysis. A more accurate molecular level understanding of the catalyzed reaction mechanism will enable the determination of superior catalyst alloys or even non-metal catalyst materials that provide better performance or are more cost effective than current transition metal alloys. NASA has used both hydrogen fuel cells and solid-oxide fuel cells for various applications in past missions, and the method developed here would be able to provide a greater understanding of molecular level phenomena and therefore the ability to develop superior catalyst materials for these fuel cells. This would allow for weight- and space-requirement reduction due to reduced catalyst quantities, as well as superior

A Combined Density Functional Theory and Monte Carlo Approach for Quantifying Catalytic Energies in a Liquid Environment

Table of Contents

power output and reduced fuel consumption for these fuel cells. While this project focuses on fuel cells, it will be readily adaptable to any heterogeneously catalyzed reaction system with a fluid feed. Heterogeneous catalysis is also ubiquitous in industrial applications, and the knowledge gained from this project would be easily ported to have a widespread effect by enabling a more comprehensive study of optimal catalyst materials for these purposes.

Anticipated Benefits

This work will prove significant because it will yield a method that will be able to yield simulation results that provide a more accurate picture of molecular scale phenomena affecting heterogeneous catalysis. A more accurate molecular level understanding of the catalyzed reaction mechanism will enable the determination of superior catalyst alloys or even non-metal catalyst materials that provide better performance or are more cost effective than current transition metal alloys. NASA has used both hydrogen fuel cells and solid-oxide fuel cells for various applications in past missions, and the method developed here would be able to provide a greater understanding of molecular level phenomena and therefore the ability to develop superior catalyst materials for these fuel cells. This would allow for weight- and space-requirement reduction due to reduced catalyst quantities, as well as superior power output and reduced fuel consumption for these fuel cells. While this project focuses on fuel cells, it will be readily adaptable to any heterogeneously catalyzed reaction system with a fluid feed. Heterogeneous catalysis is also ubiquitous in industrial applications, and the knowledge gained from this project would be easily ported to have a widespread effect by enabling a more comprehensive study of optimal catalyst materials for these purposes.

Organizational Responsibility

Responsible Mission Directorate:

Space Technology Mission Directorate (STMD)

Lead Organization:

Clemson University

Responsible Program:

Space Technology Research Grants

Project Management

Program Director:

Claudia M Meyer

Program Manager:

Hung D Nguyen

Principal Investigator:

Rachel Getman

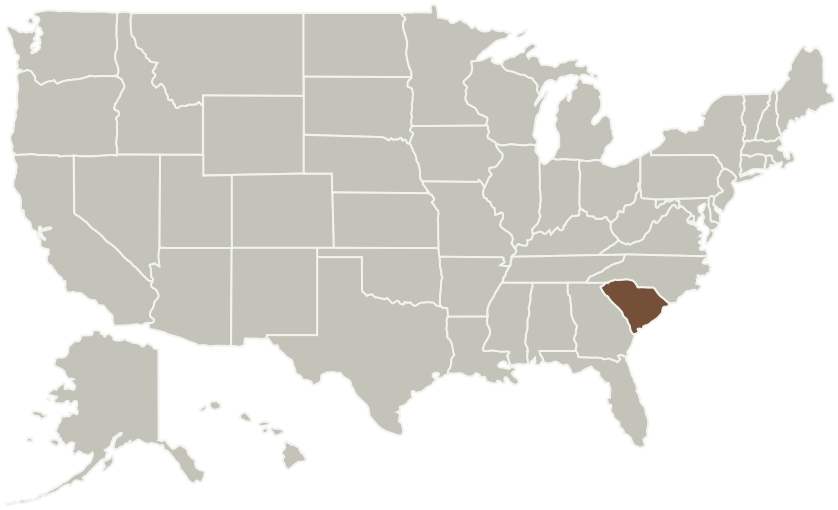
Co-Investigator:

Cameron J Bodenschatz

A Combined Density Functional Theory and Monte Carlo Approach for Quantifying Catalytic Energies in a Liquid Environment

Completed Technology Project (2014 - 2018)

Primary U.S. Work Locations and Key Partners



Organizations Performing Work	Role	Type	Location
Clemson University	Lead Organization	Academia	Clemson, South Carolina

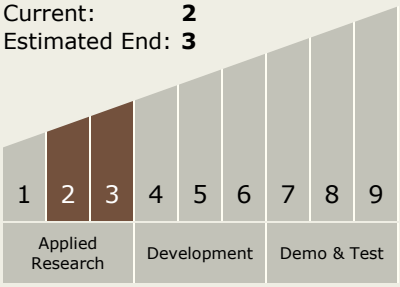
Primary U.S. Work Locations
South Carolina

Project Website:

https://www.nasa.gov/directorates/spacetech/home/index.html

Technology Maturity (TRL)

Start: **2**
Current: **2**
Estimated End: **3**



Technology Areas

Primary:

- TX03 Aerospace Power and Energy Storage
  - TX03.2 Energy Storage
    - TX03.2.2 Electrochemical: Fuel Cells

Target Destinations

Earth, Others Inside the Solar System, Foundational Knowledge